

# REDUCING THE VOLUME AND WEIGHT OF THE FUEL POST PROCESSOR FOR POLYMER ELECTROLYTE FUEL CELL POWER SYSTEMS

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## Introduction

Polymer electrolyte fuel cell (PEFC) systems are a leading candidate for replacing the internal combustion engine in light-duty vehicles. One method of generating the hydrogen necessary for the PEFC is reforming a liquid hydrocarbon, such as methanol or gasoline, via partial oxidation, steam reforming, or a combination of partial oxidation and steam reforming (referred to as "autothermal reforming"). The H<sub>2</sub>-rich product gas, termed "reformat," can contain as much as 10% carbon monoxide (CO). In addition, if sulfur is present in the liquid hydrocarbon, it is converted to hydrogen sulfide (H<sub>2</sub>S). Autothermal reforming of a gasoline with a sulfur content of 30-80 ppm will produce a reformat containing 3-8 ppm H<sub>2</sub>S. Both CO and H<sub>2</sub>S have been shown to poison the platinum-based anode catalyst at concentrations of <100 ppm and <1 ppm, respectively [1], and therefore, the concentration of CO and H<sub>2</sub>S in reformat must be reduced prior to passing the reformat to the fuel cell stack. We are developing new catalysts and adsorbents for achieving the desired CO and H<sub>2</sub>S concentrations in the reformat.

## CO Reduction Using Existing Technologies

To reduce the bulk of CO concentration in reformat, the water-gas shift (WGS) reaction,  $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ , is used to convert the bulk of the CO to CO<sub>2</sub>, with the equilibrium CO concentration decreasing with decreasing temperature. To maintain a sufficient rate of reaction, the WGS reactor is maintained at temperatures above 200°C, which limits the concentration that CO can be reduced to 2000-5000 ppm. Industrially, the WGS reaction is conducted with two catalysts, which operate in different temperature regimes. One catalyst is a FeCr oxide, which operates at 350-450°C and is termed the high-temperature shift (HTS) catalyst. The second catalyst is a CuZn oxide, which operates at 200-250°C and is termed the low-temperature shift (LTS) catalyst. Although these two catalysts are used industrially in the production of H<sub>2</sub> for ammonia synthesis, they have two major drawbacks that make them unsuitable for transportation applications. The first is the relatively low activity of these catalysts, which results in the WGS reactor being the largest reactor in the fuel processing train in terms of volume/weight. The second is the need to activate these catalysts by *in situ* reduction and to maintain them in a reduced state to maintain activity. Achieving those conditions will be challenging given the highly intermittent duty cycles experienced in transportation applications. Therefore, we are developing new WGS catalysts that (1) increase the activity and thereby

reduce the volume/weight of the shift reactor, (2) eliminate the need to activate the catalyst *in situ*, (3) eliminate the need to sequester the catalyst under non-oxidizing conditions during system shutdown, and (4) do not sinter during temperature excursions.

To reduce the CO concentration in the reformat after the WGS shift reaction to <100 ppm, we are investigating a number of technologies including preferential oxidation (PrOX) of CO to CO<sub>2</sub> in the presence of H<sub>2</sub>, CO adsorption, and membrane separations. We will not discuss these technologies in this paper.

## **H<sub>2</sub>S Removal Using Existing Technologies**

One approach to removing H<sub>2</sub>S from reformat is to react it with ZnO to form ZnS,  $\text{H}_2\text{S} + \text{ZnO} \leftrightarrow \text{ZnS} + \text{H}_2\text{O}$ . An equilibrium concentration of H<sub>2</sub>S < 1 ppm can be achieved at temperatures below 400°C for H<sub>2</sub>O vapor concentrations typically found in reformat. Commercially, ZnO is available from catalyst manufacturers, primarily in the form of extrudates. These ZnO extrudates are used in manufacturing processes, such as ammonia synthesis, and are designed to operate at relatively low gas hourly space velocities (i.e., <2000 h<sup>-1</sup>) but with high sulfur weight loadings (up to 25 wt%). For reformat with an average H<sub>2</sub>S concentration of 30 ppm, the weight of ZnO extrudates required is estimated to be ~31 kg based on manufacturer's specifications. This weight is impractical for transportation applications. Furthermore, with the new reduced sulfur content gasolines, only a small fraction of the ZnO would be utilized during the expected lifetime of the fuel processor. Therefore, we are investigating new structured forms of ZnO to improve the rate of H<sub>2</sub>S removal and increase the utilization of ZnO.

## **Development of New Water-Gas Shift Catalysts**

From a mechanistic viewpoint, no single metal, with the exception of copper, has high activity for both the dissociation of H<sub>2</sub>O and oxidation of CO, two important elementary reaction steps for the water-gas shift reaction. Therefore, we are investigating bifunctional catalysts where one component of the catalyst promotes the adsorption or oxidation of CO and the other component dissociates the H<sub>2</sub>O. Our current research is focusing on identifying metal-support combinations to promote this bifunctional mechanism. Candidate metals (Pt, Ru, Pd, PtRu, PtCu, Co, Ag, Fe, Cu, Mo) were selected based on the heat of adsorption of CO. Candidate oxide supports (lanthanide oxides, manganese oxide, vanadium oxide) were selected based on their redox properties and their ability to adsorb and dissociate H<sub>2</sub>O under highly reducing conditions.

Our initial work focused on a Pt/mixed-valence oxide catalyst (ANL-1) dispersed on a high-surface area alumina. Compared to the commercial FeCr and CuZn oxide catalysts, this catalyst does not have to be activated by *in situ* reduction, does not lose its activity upon exposure to air at 21-550°C, and is active over a wide temperature range (180-400°C). The high cost of the noble metal Pt, however, may limit the use of this catalyst in transportation applications. To address the cost issue, we are investigating less costly non-precious metals to replace Pt. As shown in Fig. 1, a non-precious metal/mixed oxide catalyst (ANL-2) exhibits WGS activity comparable to ANL-1. Although ANL-2 is not as active as the commercial CuZn oxide catalyst (United Catalysts Inc. C18-7), it does not exhibit a loss in activity after exposure to air at 230°C (Fig. 2).

Table 1 gives the estimated volumes for a two-stage adiabatic WGS reactor in a 50 kWe fuel processor using commercial HTS and LTS catalysts, ANL-1, and ANL-2. Although the commercial CuZn oxide catalyst (UCI C18-7) is more active than ANL-1 and ANL-2 at 230°C, it rapidly loses activity when exposed to temperatures above 270°C, whereas ANL-1 and ANL-2

do not exhibit a loss in activity up to 400°C. By taking advantage of the higher temperature stability of ANL-1, a reactor using this would be ~30% smaller than a reactor using the commercial catalysts. Although a reactor using ANL-2 would be slightly larger than a reactor using the commercial catalysts, it may be possible to reduce the reactor size with further development to improve the activity of ANL-2.

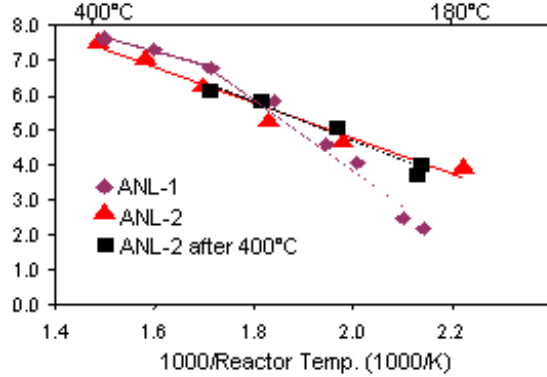


Fig. 1. Arrhenius plots for ANL-1 and ANL-2. Test conditions: 8.6%CO, 15.0% CO<sub>2</sub>, 29.7% H<sub>2</sub>, 30.9% H<sub>2</sub>O, balance N<sub>2</sub>, gas hourly space velocity (GHSV)=200,000 h<sup>-1</sup>

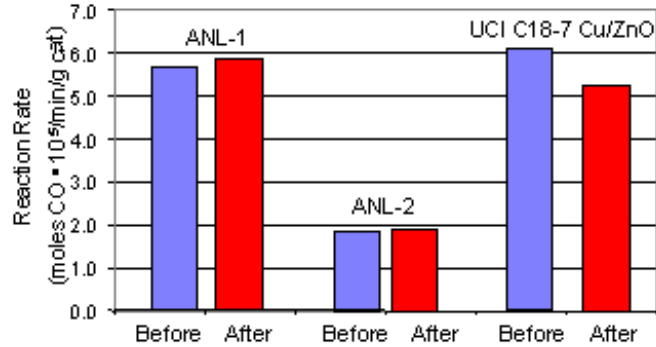


Fig. 2. Reaction rates of ANL-1, ANL-2, and commercial CuZn oxide catalysts before and after exposure to air at 230°C. Test conditions: 230°C, 0.45% CO, 11.3% CO<sub>2</sub>, 22.3% H<sub>2</sub>, 55% H<sub>2</sub>O, bal. N<sub>2</sub>, GHSV=200,000 h<sup>-1</sup>

Table 1. Estimated volumes of a two-stage adiabatic WGS reactor to reduce the CO concentration in reformat to 1% (dry basis). Reformate composition is 10% CO, 10% CO<sub>2</sub>, 34% H<sub>2</sub>, 13% H<sub>2</sub>O, bal. N<sub>2</sub>. The reactor volume is estimated using experimentally measured intrinsic reaction rates and activation energies for ANL-1 and ANL-2, and published kinetic data for the commercial catalysts [2].

Catalyst	Commercial Fe/Cr and Cu/Zn Oxides		ANL-1		ANL-2	
	HTS	LTS	HTS	LTS	HTS	LTS
T <sub>in</sub> , °C	400	200	400	300	400	300
T <sub>out</sub> , °C	455	227	455	327	457	327
CO <sub>in</sub> , %	11.4	4.3	11.4	4.3	11.4	4.3
CO <sub>out</sub> , %	4.3	1.0	4.3	1.0	4.3	1
Vol, L	5.5	13.7	0.8	12.7	2.8	18.4
Total, L	19.2		13.5		21.2	

To maximize the efficiency of the fuel processing train, the WGS and ProX reactors, as well as the sulfur removal unit (which will be discussed below), are thermally integrated with the fuel reformer. As a consequence of this thermal integration, the WGS reactor could be designed to operate as a single-stage reactor with a declining temperature profile instead of a two-stage adiabatic reactor. There are several advantages to operating the WGS reactor as a single stage with a declining temperature profile including a high reaction rate in the higher temperature region of the reactor, where the equilibrium is unfavorable, and a larger reaction driving force at the lower temperature region, where equilibrium is more favorable. The temperature profile in the WGS reactor is maintained by the water and air feeds to the reformer, which in our current design flow countercurrent to the reformat flow in the WGS reactor. Figure 3 shows the optimal temperature profile and the corresponding concentration of CO in reformat for the WGS

reactor as a function of the normalized reactor length. We can experimentally approximate a declining temperature reactor by using a series of isothermal reactors, with each reactor operating at a lower temperature than the preceding reactor, as shown in Fig. 3. While such a configuration approximates the behavior of a single declining temperature reactor, the cumulative volume of a series of isothermal reactors is larger than that of a single declining temperature reactor to achieve the same level of conversion.

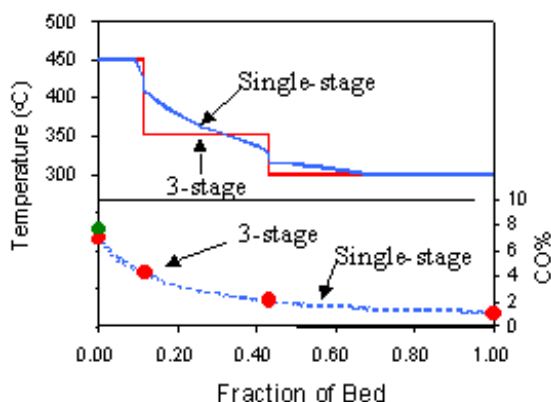


Fig. 3. Temperature profile and concentration of CO as a function of reactor bed length for a single-stage, declining-temperature WGS reactor and a 3-stage isothermal WGS reactor.

## Development of Structured Forms of ZnO for Sulfur Removal

To improve the performance of ZnO, in terms of higher space velocities, as well as increased utilization of ZnO, we are investigating the use of thin layers (50-100  $\mu\text{m}$ ) of ZnO, coated onto a monolith (Fig. 4) or as a self-supporting ZnO structure (Fig. 5). Initial testing has shown that the self-supporting ZnO structure can reduce the  $\text{H}_2\text{S}$  concentration in a simulated reformat from 10-30 ppm to < 1 ppm at a space velocity of  $8000\text{ h}^{-1}$ . We also estimated that a ZnO-coated monolith can reduce the weight of the ZnO bed to ~5-6 kg, which is ~80-85% less weight compared to ZnO bed using extrudates.

## Conclusions

We have developed a WGS catalyst composed of Pt/mixed-valence oxide that is potentially better suited than existing FeCr and CuZn oxide catalysts for fuel processing conditions in transportation applications and will significantly reduce the volume of the shift reactor. Because of concern over the high cost and limited supply of Pt, we have also begun developing on a non-precious metal/mixed-valence WGS catalyst. A ZnO-coated monolith and a self-supporting ZnO structure have been shown to reduce the concentration of  $\text{H}_2\text{S}$  in synthetic reformat below 1 ppm. It is estimated that these structured forms of ZnO have the potential to significantly reduce the volume/weight of the sulfur removal bed compared to ZnO extrudates.



Fig. 4. ZnO-coated cordierite monolith.



Fig. 5. Micrograph of self-supporting ZnO layer.

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## **References**

1. T. Zawodzinski, J. Bauman, T. Rockward, B. Mueller, T. Springer, F. Uribe, J. Valerio, and S. Gottesfeld, "R&D on Optimized Cell Performance for Operation on Reformate and Air," Presented at DOE Fuel Cells for Transportation National Laboratory R&D Meeting, June 23-25, 1999, Argonne, IL.
2. R. L. Keiski, O. Desponds, Y.-F. Chang, and G. A. Somorjai, *Applied Catalysis A: General*, Vol. 101, pp. 317-318, 1993.